# Selective oxidation of methane to methanol with molecular oxygen using aqueous Au-Pd colloids at low temperature

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**Abstract:** The selective oxidation of methane remains a major challenge for catalysis. Using colloidal gold-palladium nanoparticles rather than supported AuPd nanoparticles, we show that methane can be selectively oxidised to methanol with high selectivity (92%) in aqueous solution at mild temperatures (27-50 $^oC$). Using isotopically labeled $^{18}O_2$ as an oxidant in the presence of $H_2{}^{18}O_2$, we demonstrate that the methanol produced incorporated a substantial fraction (70%) of gas-phase $O_2$. In this reaction the $H_2O_2$ acts as an initiator but more oxygenated products were formed than $H_2O_2$ consumed, suggesting that the controlled breakdown of $H_2O_2$ activates methane which subsequently incorporates molecular oxygen through a radical process.

**Keywords:** methane oxidation, methanol.

## 1. Introduction

The direct oxidation of methane to methanol remains a key challenge. Many approaches have been suggested to date. The industrial methanol production is an energy-intensive and an indirect process that converts methane to synthesis gas before further conversion to methanol and other bulk chemicals. However, over the decades this process has been fully optimised. Recently there has been an interest in shale gas which is highly distributed and is often found in remote locations. A strategy is needed to liquefy this natural gas and conversion to methanol presents an opportunity to develop new catalytic approaches well suited to smaller point sources of natural gas. In this presentation we will demonstrate one such approach that may have potential.[1]

## 2. Experimental (or Theoretical)

Bimetallic Au-Pd nanoparticles were prepared by standard colloidal methods. An aqueous solution of $HAuCl_4$ precursor (Sigma Aldrich) and acidic solution of $PdCl_2$ (Sigma Aldrich) precursor (in 0.5 M HCl) were dissolved in 800 mL of de-ionized water to give a total metal concentration of 0.16 mmol / L. Polyvinylpyrrolidone (PVP, average molecular weight 1,300,000, Sigma Aldrich) was added as a stabilizer to give the required metal-to-PVP ratio (typically 1:1.2). After 2-3 min of stirring, freshly prepared 0.1 M sodium borohydride ($NaBH_4$, Sigma Aldrich) solution was added such that the molar ratio of $NaBH_4$-to-metal was 5. The required 6.6 ml of 0.1M $NaBH_4$ was added as two 3.3 ml aliquots. This produced a dark brown colloid which was the left stirring for 30 minutes to ensure all the metal precursors were reduced to metallic form. The colloid was concentrated using a roto-evaporator to give a nominal metal loading of 0.66 mmol / L. Methane oxidation was carried out in a 50 mL glass-lined stainless steel Parr autoclave reactor. The reactor was charged with 10 mL of colloidal catalyst (6.6 µmol metal equivalent) and different amounts of $H_2O_2$ (Sigma Aldrich, 50% wt in water). The charged autoclave was sealed and purged three times with methane (99.999%, Air Products). It was then pressurized with methane (30 bar) and oxygen (5 bar, BOC) to remain within oxygen lean reaction limits. The mixture was stirred at 1500 rpm and heated to the desired reaction temperature (usually 50ºC) at the ramp rate of 2.25 °C/min and maintained at the reaction temperature for a fixed time (usually 30 min). At the end of reaction, the autoclave was cooled in ice to a temperature below 10ºC in order to minimize the loss of volatile products. The reaction gas was removed for analysis in a gas sampling bag. For isotopic reactions, BOC specialty gases > = 98% $^{18}O$ enriched $O_2$ gas and > = 98% $^{13}C$ enriched $CH_4$ were used. Product analysis was carried out using $^1H$-NMR with a

Bruker 500 MHz NMR equipped with a solvent suppression system. It was used to quantify the amounts of liquid phase products using TMS in $CDCl_3$ as an internal standard.

## 3. Results and discussion

In the methane oxidation experiments we first used $H_2O_2$ as an oxidant at 50ºC and we found that when the unsupported AuPd colloid was used as a catalyst the level of decomposition of $H_2O_2$ was much lower than when the AuPd colloid was supported on $TiO_2$. In view of this the products observed with the unsupported catalyst were substantial (Figure 1a). However, when molecular oxygen was added to the reaction gases the amount of products observed increased markedly (Figure 1b). Use of isotopically labelled $^{18}O_2$ showed that up to 70% of the methanol contained oxygen from the molecular oxygen. In this reaction the $H_2O_2$ acts as an initiator but more oxygenated products were formed than $H_2O_2$ consumed, suggesting that the controlled breakdown of $H_2O_2$ activates methane which subsequently incorporates molecular oxygen through a radical process.

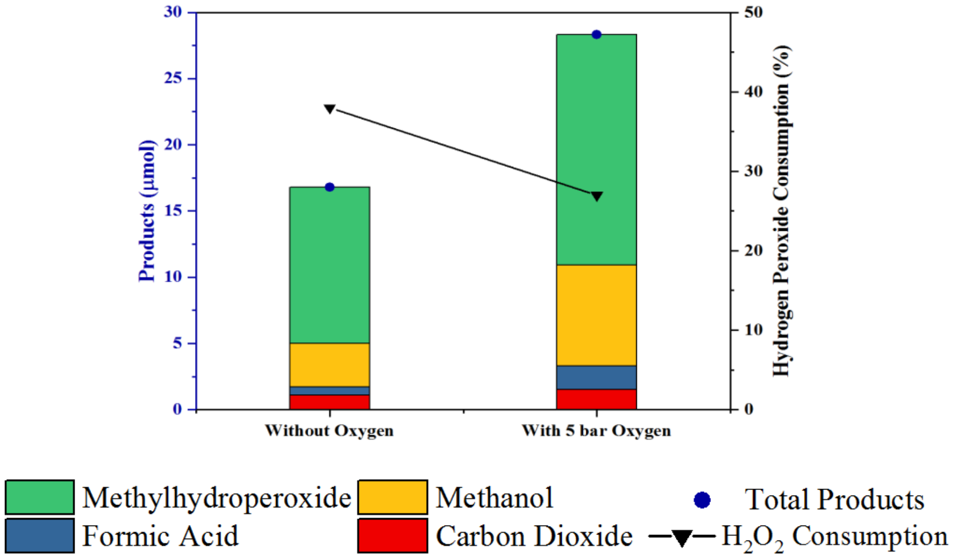

**Figure 1.** Conversion of methane using unsupported AuPd colloid. 0.5 h, 50ºC, $H_2O_2$ amount: 1000 µmol, 1500 rpm, stirred ramping, $P(CH_4)$ = 30 bar, $P(O_2)$ = 5 bar, 6.6 µmol metal per reaction

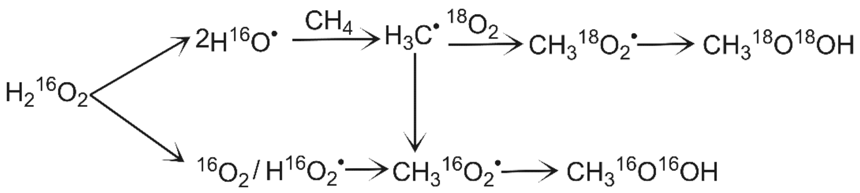

**Figure 2.** Proposed reaction mechanism.

## 4. Conclusions

Using unsupported AuPd colloids with $H_2O_2$ as an initiator together with $O_2$, methane can be oxidized to methanol where the oxygen in the methanol is derived from $O_2$.

## References

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